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(54) ELECTROLYTIC METHOD AND TREATMENT BATH FOR PROVIDING CHROMIUM-CONTAINING PROTECTIVE COATINGS ON STEEL STOCK

(71) We, UNITED STATES STEEL CORPORATION, a corporation organized and existing under the laws of the State of Delaware, United States of America, doing business at 525 William Penn Place, Pittsburg, State of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention pertains to chromium-containing electrolytes and the use thereof for the production of coated, corrosion-resistant flat-rolled steel based stock.

Flat-rolled steel has long been produced with an overlying layer of tin, either applied by hot dipping or, more recently, by electrodeposition. The tin layer serves as a protective, corrosion-resistant coating of particular value when the thus-coated steel is used in the manufacture of food and beverage cans and other containers required a corrosion-resistant surface. The tin layer also facilitates soldering of the side seam construction usually employed in the manufacture of such articles.

More recently, such containers have been produced by welding or by adhesive bonding of the side seam, thus enabling elimination of the tin layer required for effective soldering. Elimination of the costly tin layer is, of course, of considerable economic advantage.

Untinned flat rolled steel stock, when used for can-making purposes, must be provided with a protective coating, such as enamel or lacquer, to prevent deleterious chemical reaction between corrosive can contents and the metal can body. Such protective coatings are of a variety of compositions, being specific in nature and function to the intended application of the coated container, and are preferably applied to the flat metal container stock by the container manufacturer, rather than by the steel producer.

Since the uncoated flat-rolled steel is

susceptible to rusting during extended periods of shipment and storage, and since rusting detracts from the desired clean, bright appearance of the steel and also deleteriously affects adherence of subsequently applied protective coatings, rusting should ideally be prevented and the steel delivered to the container manufacturer in a suitable condition for application and retention of the necessary protective coatings even after considerable periods of storage under humid conditions. Further, since the latter coatings are generally transparent, any treatment of the steel by the steel producer preferably should not detract from the desired bright metallic appearance of the finished fabricated article.

Additionally, the metal stock provided to the can manufacturer should preferably be of such a nature as to resist delamination of the subsequently applied enamel or lacquer coating during fabrication, and the stock should preferably resist undercutting of such overlying protective coating by corrosive action of the can contents at the sites of defects in the enamel or lacquer coating or breaks, cuts or other defects caused during container fabrication.

Still further, in the case of containers having an adhesively bonded lapped side seam, it is usually required by the container manufacturer that such bond have a minimum peel (separation) strength of 25 pounds per inch of seam width for steel stock of 55 to 60 pounds basis weight (about 6 to 7 mils thickness).

Ordinary, untreated, cleaned and oiled flat-rolled steel (black plate) does not satisfy all of the foregoing requirements.

Most recently, tin-free steels have been made available for container manufacture and which provide, on the flat-rolled steel surface, either a thin layer of electrolytically deposited metallic chromium (see for example, U.S. Patent Specification No. 3,113,845), a film of chromium-containing oxides (see for example, U.S. Patent Specifi-

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cation No. 2,998,361), or both (see for example, U.S. Patent Specification No. 3,296,100).

However, electroplating processes have been inherently costly whereas, for their successful use in production of stock for container manufacture, they should ideally add only insignificantly to the cost of production of untreated black plate.

Specifically, such electrolytic processes, to be of maximum commercial utility and value, should ideally meet the following economic criteria:

1. the cost of the electrolytic bath chemicals must be low;
2. the concentration of the bath chemicals must be low in order to avoid economic loss due to high dragout losses at the normally required high line speeds, e.g. 500 to 1500 feet per minute or greater;
3. the bath treating time must be low, in order to reduce to an economically feasible number, the treating tanks required;
4. the power requirements must be low;
5. the bath composition must be uncomplicated in preparation, control and maintenance;
6. the process must be sufficiently flexible in operation, so that only minor changes in process conditions need be made to produce a wide range of products of optimum characteristics for many end-use applications; and
7. the overall process must be susceptible of easy and accurate control to ensure optimum product quality without excessive post-production and pre-fabrication quality testing.

The prior art, such as that referred to above, does not provide processes which have enough of the foregoing desirable attributes and which also provide products having enough of the aforementioned desirable property characteristics. For example, although U.S. Patent No. 3,296,100 teaches the production of articles comprising a steel base, such as flat-rolled can stock steel, provided with an intermediate, thin metallic chromium layer and an overlying chromium oxide film, by a process using a low concentration (10—50 g/l) of chromic acid plus a sulfuric acid radical catalyst, a pre-treatment of the bath by electrolysis is taught as required to provide a certain proportion of trivalent chromium ions in the bath solution. U.S. Patent No. 3,113,845 teaches production of a thin metallic chromium layer on steel, such as can stock, by means of an electrolytic bath wherein the chromic acid content, as is usual in most prior art chromium plating baths, is relatively high e.g. 100—250 g/l. U.S. Patent No. 2,998,361 teaches the

production of hydrated chromium oxide films only, the formation of such films being promoted by the use of aromatic sulfonic acids and sulfonates, in a chromic acid-containing electrochemical bath.

Chromium deposition, in thin layers on can stock steel, has also been effected from electrochemical baths containing, as the metallic chromium-depositing promoter or catalyst, phosphoric acid, boric acid and oxalic acid (U.S. Patent No. 3,032,487). The necessity of boiling the oxalic acid-containing bath until oxidation of the latter compound is complete, is a further illustration of a costly, time-consuming procedure which detracts from the commercial value of prior art processes.

Expensive and hard-to-handle fluorine-containing compounds, such as hydrofluoric acid and silicofluoric acid, have also been used in the prior art, in conjunction with usual metallic chromium-depositing catalysts, such as sulfuric acid and sulfates, to promote production of bright chromium plate.

The present invention provides a method for the continuous production of coated corrosion-resistant, flat-rolled steel-base stock comprising continuously passing a flat-rolled steel-base stock through an electrochemical treating bath comprising an aqueous solution containing from 5 to 80 g/l of chromium trioxide and from 0.25 to 5 g/l of a promoter material selected from cobaltous chloride calculated as the hexahydrate and sulfamic acid, while employing the stock as cathode for the bath to provide the stock with a protective coating comprising a layer of metallic chromium adjacent to the stock surface and a layer of hydrated chromium oxide overlying the metallic chromium layer. The preferred concentration of chromium trioxide is from 15 to 25 g/l; the bath preferably contains from 0.25 to 1.0 g/l of cobaltous chloride (calculated as the hexahydrate) or from 0.25 to 2.0 g/l of sulfamic acid. The preferred bath temperature is from 70° to 190°F.

The present invention also provides an electrochemical treatment bath comprising an aqueous solution containing from 5 to 80 g/l of chromium trioxide, and from 0.25 to 5 g/l of a promoter selected from cobaltous chloride (calculated as the hexahydrate) and sulfamic acid. Chromium trioxide, the chromium containing constituent of the bath, is readily available and of low cost, and is employed in a relatively low concentration; the bath does not require pre-treatment.

All amounts quoted for cobaltous chloride herein are calculated on the basis that the cobaltous chloride is in the hexahydrate form.

A preferred embodiment of the bath according to the invention contains from 15 to 25 grams per liter (g/l) of chromium tri-

oxide (CrO_3), and from 0.25 to 1.0 g/l of cobaltous chloride (calculated as $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), or from 0.25 to 2.0 g/l of sulfamic acid ($\text{H}_2\text{NSO}_3\text{H}$). One embodiment of the method according to the invention is conducted by maintaining such a bath at a temperature of from 70° to 190°F , and passing continuously therethrough a cleaned carbon steel strip, as cathode, for a residence time in the bath of from 0.25 second to 10 seconds, at a cathodic current density of from 25 to 300 amperes per square foot (asf), to provide an input to the cathode of from 50 to 1000 coulombs per square foot (coulombs/ ft^2) of electrical energy.

The chromium layer formed according to the invention preferably ranges in weight from 0.1 to 2.0 mg of metallic chromium per square foot of stock surface, and the hydrated chromium oxide layer preferably contains from 0.1 to 30 mg, most preferably from 0.1 to 15 mg, of chromium values per square foot of stock surface.

Among those knowledgeable in the art of metal surface treatment, it is well known that steel from different coils, such as coils of flat-rolled steel of can-stock gauges, e.g. 5 to 10 mils in thickness, even if ostensibly produced in the same manner, and by means of the same equipment, will frequently have quite different surface characteristics, so that a given surface treatment, applied to such coils, will produce markedly different results. Obviously, then, any surface treatment such as an electrolytic treatment, in order to provide an altered steel surface of the desired uniform properties, must be capable of fast and accurate response to variations. The action of the electrochemical baths of this invention is sufficiently fast in operation and consistent in result produced under a given set of operating conditions, e.g. current density, and those conditions are so readily and quickly changed in response to a change in surface reactivity of steel being treated, that the invention can be practised under a wide range of conditions, to produce a usefully wide range of products, each of which is predictably consistent in properties. Indeed, the operating conditions of the process of the invention are sufficiently flexible that the invention can be practised with existing continuous steel strip electroplating facilities with only minor changes, if any.

In accordance with the process of the invention, the stock, e.g. plain carbon steel black plate, can be subjected to usual pre-plating cleaning steps, e.g. electrolytic alkaline treatment, rinse, cathodic acid treatment and rinse; the stock is then introduced, as cathode, and in continuous fashion, between insoluble, e.g. lead, anodes into the electrochemical treatment bath of the invention. The acid pre-treatment may be omitted.

Treating time in the bath according to

the invention is most usually between 0.25 and 10 seconds, although bath residence times of 3 seconds and under are preferred for economic reasons and are sufficient for the application of most coatings for can fabrication purposes.

The current density applied to the cathodic strip in the treating bath preferably ranges from 25 to 300 asf, since below 25 asf insufficient coating coverage may be experienced, and best chromium plating efficiencies, bright metallic chromium surfaces, and optimum oxide production is not realized at current densities over 300 asf.

Residence time of the strip in the bath and magnitude of the applied current density are preferably selected within the above-provided ranges of each such that the total coulombic input to the strip in the bath is from 50 to 1000 coulombs/ ft^2 .

The bath temperature is preferably maintained from 70° to 190°F in order to maintain best strip coating efficiency and to maintain a bright metallic appearance of the chromium layer.

As a part of the cleaning pre-treatment, the stack to be electrochemically treated in the aforesaid bath may beneficially be given an anodic flash treatment prior to entry of the steel article into the coating bath. It has been found that adherence of the subsequently produced chromium oxide film is greatly improved by such treatment, thus inhibiting removal or disruption of such oxide film in the course of post-plating operations, or by rolls. Such anodic pre-treatment is most conveniently accomplished by immersing the stack, as anode, in a first pass zone containing the same electrolyte as used for the following plating treatment. Such operation avoids contamination of the plating bath electrolyte and eliminates the necessity of providing a separate pre-treatment tank. However, such other tanks, and other electrolytes could be used if desired. The anodic current density applied does not affect the quantity of metallic chromium or hydrated chromium oxide deposited in the electrochemical coating bath zone, and the magnitude and duration of such anodic current density application need be only sufficient to effect the aforesaid oxide film adherence enhancement.

Various post-coating treating steps may also be used, if desired, to impart additional or enhanced product characteristics, such as further enhancement of rust resistance, e.g. when most dilute chromium trioxide solutions are used in the electrochemical coating bath.

The double-layered coating applied in the electrochemical coating bath of the invention comprises a layer of metallic chromium deposited on the stock surface and a film or layer of hydrated chromium oxides over-

lying the metallic chromium layer. Since this double-layered coating is formed in a single electrochemical treating zone, it is postulated that both layers form simultaneously and continuously, part of the chromium values in the bath being reduced to metallic chromium and a portion being incompletely reduced and forming the overlying hydrated chromium oxides, although the invention is not limited to this proposed explanation.

The metallic chromium layer so produced preferably ranges in weight from 0.1 to 2.0 mg of metallic chromium per square foot of surface, and the overlying hydrated chromium oxide film from 0.1 to 30 mg of chromium values (Cr^{+++}) per square foot of surface. The most preferred coatings are those wherein the metallic chromium layer is from 0.20 to 1.5 mg of metallic chromium per square foot and the hydrated chromium oxide layer contains from 2.0 to 15.0 mg of chromium values per square foot.

The most useful coatings are those wherein the hydrated chromium oxide film is so thin, generally under 15 mg of chromium per square foot, that the film produces an interference color on the surface of the treated article, imparting to the article a most pleasing and beautiful appearance. By varying the oxide film thickness, a wide range of colors can be produced. Color change is very sharp and sensitive to oxide film thickness, an oxide film thickness change of only about 2.0 mg $\text{Cr}^{+++}/\text{ft}^2$ causing a change in color from deep violet to light blue. Thus, the same appearance and hence the same thickness of hydrated oxide coating can be imparted to each coil of steel treated regardless of its original surface reactivity, or a hydrated oxide film of predetermined thickness can be applied to the stock by merely adjusting the coulombic treating level until the desired color, corresponding to a certain chromium oxide film thickness, is obtained. The desired color can be produced by detecting color changes in the treated stock either visually or by suitable optical instrumentation, and coulombic input to the stock in the electrochemical coating bath can then be varied manually or automatically, in accordance with the detected color changes. These colors, being interference colors, disappear after application of the final lacquer coating by the can manufacturer and do not then alter the metallic appearance of the metallic chromium layer as seen through a transparent lacquer coating.

The following specific examples are illustrative of the electrochemical coating baths and the method of the invention.

Example 1

Commercially produced, double cold-reduced plain carbon steel of 60 pound basis weight gauge (6.7 mils thickness), was given

a pre-plating processing common to tin-plating quality black plate (except for acid pickling), i.e., it was electrolytically cleaned in alkaline solution and water rinsed. It was then given an anodic flash, at a current density of 170 asf for 0.67 second (114 coulombs/ ft^2), in an electrochemical treating tank (containing the same electrolytic bath as given below). The cleaned strip was then treated in an aqueous electrochemical coating bath as follows:

Process Element	Element Specification	
chromium trioxide, CrO_3	60 g/l	
cobaltous chloride, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	0.5 g/l	80
cathodic current density	170 asf	
cathodic treating time	2.0 seconds	
solution temperature	120° F	
line speed	150 fpm	
coulombs per square foot (cathodic pass)	340	85

Example 2

Steel strip similar to that of Example 1 was given the same pretreatment, except that the anodic flash was at a current density of 87 asf (58 coulombs/ ft^2), and then cathodically treated in an aqueous bath as follows:

Process Element	Element Specification	
chromium trioxide	20 g/l	95
sulfamic acid	1.0 g/l	
cathodic current density	100 asf	
cathodic treating time	2.0 seconds	
solution temperature	140° F	
line speed	150 fpm	100
coulombs per square foot (cathodic pass)	200	

Example 3

Steel strip similar to that of Examples 1 and 2 was given the same pretreatment, except that the anodic flash was for 1.0 second at a current density of 85 asf (85 coulombs/ ft^2), and then cathodically treated in an aqueous bath as follows:

Process Element	Element Specification	
chromium trioxide	5.0 g/l	
cobaltous chloride	0.25 g/l	
cathodic current density	127 asf	
cathodic treating time	3.0 seconds	115
solution temperature	120° F	
line speed	100 fpm	
coulombs per square foot (cathodic pass)	381	

In this Example 3, following the electrochemical coating treatment, the coated strip was rinsed, "squeegeed", and then passed into an aqueous chemical treating bath containing 10 g/l of chromium trioxide, the strip was then again "squeegeed" and hot air dried.

The products produced by the use of the aforesaid exemplary electrochemical coating

baths and processes, including weights of metallic chromium and hydrated chromium oxide layers produced, together with performance of those products when tested for can fabrication property requirements in accordance with certain test procedures (as hereinafter described), are given in Table I below.

TABLE I

Example No.	Chromium, mg/ft ²		Metallic Cr Layer		Oxide Layer		Peel Strength, lbs. per $\frac{1}{2}$ inch of seam width		Enamel Process Adhesion 1-hour Test (1)		Citric Acid Test, line width, mm		Humid Storage Test, 30 Day		Stack Rust Test, 60 Day	
	Top		Bottom		Top		Average of Top & Bottom		Top		Top		Day		Grade (2)	
	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom
1	0.8	0.4	6.3	5.4			26		0	0	0.1	0.1	0	0	0	0
2	0.5	0.5	8.3	6.8			31		0	0	0.1	0.1	0	0	3	3
3	0.5	0.4	5.4	4.3			39		0	0	0.1	0.1	1	1	2	2

(1) 0 = no enamel removed
10 = all enamel removed

(2) 0 = no rust
10 = heavy rust

It will be seen from Table I that both a metallic chromium layer and an overlying chromium oxide layer was produced in the case of each of the above three exemplary processes of the invention, the metallic layer comprising from 0.4 to 0.8 mg Cr/ft², and the oxide layer comprising from 4.3 to 8.3 mg Cr⁺⁺⁺/ft² of treated article surface.

- 5 The products of the aforesaid examples of the process of the invention were tested to determine their conformity to the necessary product characteristics, as above-described, for food and beverage container use, the test procedures being as follows, with results as given in Table I above.

Adhesive Peel Strength Test

- 20 This test is used to measure the effect of the steel stock surface on the strength of a cemented, lapjointed side seam in tin-free steel cans.

- 25 In accordance with this test, flat panel samples (4 × 6 inches) of the treated steel stock were dip-coated with a lacquer to be used as the protective coating on the fabricated can and for which the adhesion to the can stock was to be determined.

- 30 Such lacquered panels were air dried for 10 minutes at room temperature and then oven-cured at 415°F for 30 minutes.

- 35 The panels were then cut into $\frac{1}{2}$ inch wide strips. Three nylon 11 pellets were heat-tacked to one of the lacquered strips for each of the treated steels to be tested, near one end thereof and equally spaced across the width of the strip. Another strip was positioned over the first and the two were wrapped in aluminium foil, clamped between heated (500°F) platens (slimmed apart to maintain a 3 mil adhesive layer between the bonded test strips), the pressure raised to 8000 psig and held at that value for 3 seconds. The specimens were then removed and allowed to cool at room temperature.

- 45 The strength of the resulting adhesive bond was determined by means of a standard tensile testing device provided with a special 180° peeling mandrel and operated at a speed of 2 inches per minute.

- 50 As shown by the Table I data, such tests of the products of Examples 1—3, using several proprietary can-making quality adhesives, showed the samples to have peel strengths of from 26 to 39 pounds per inch of sample width—well above the minimum 25 pounds per inch requirements for steels of such thicknesses.

Accelerated Salt water

(Enamel Process Adhesion) Test

- 60 This test is used to measure the degree of adhesion of can coating lacquers and enamels to the steel stock. Panel specimens, 4 × 6 inches, were provided with a

dip-coating of a gold phenolic lacquer (No. 1457 "Gold Lacquer", manufactured by Interchemical Corporation, of Clifton, New Jersey), thinned to give a coating weight, after baking, of 1.8—2.2 mg/in² of panel surface area.

65 The panels were air dried for 10 minutes and then oven cured for 10 minutes at 410°F.

70 The panels were then placed in an aqueous solution consisting of sodium chloride, 30 g/l, and 30% hydrogen peroxide, 10 ml/l, and maintained therein, at a temperature of 150°F, for 1 and 2 hours. The samples were then removed, rinsed in cold water, blotted dry and immediately subjected to the "Scotch Tape Test", wherein pressure-sensitive adhesive tape is applied to the sample and then quickly and forcibly removed.

80 As will be seen from the Table I data, the samples thereof, when subjected to the one hour test, showed no loss of lacquer.

Citric Acid Test

This test is used to measure the resistance of the treated steel stock to undercutting of an overlying can coating lacquer or enamel by corrosive can contents, and simulates undercutting conditions encountered at the site of scratches, breaks or holes in the lacquer on carbonated beverage cans.

90 Panels were prepared and baked in the same manner as for the accelerated salt water test. Specimens 2 inches × 4 inches were taken from the panels and the lacquer cut through with a knife, making lines of 0.1 mm width and extending (1) in the steel rolling direction, (2) across the rolling direction, and (3) diagonally to the rolling direction. The specimens were then placed, with the cut line face up, in enameled tray containing a 3% citric acid solution, and stored for 96 hours at 75 to 80°F. The specimens were then removed, blotted dry, and the total width of the cut lines was measured with a 7 magnifying glass having an 0.1 mm scale on its field.

100 Increase in scratched line width to more than 0.2 mm is considered as excessively severe undercutting.

105 From the Table I data, it will be seen that in no instance did the width of the specimen lines increase measurably.

Humid Storage Rust Resistance Test

110 This test is used to determine the resistance of steel can stock to rusting during storage in a humid atmosphere and is thus a measure of the usefulness of a surface treatment to inhibit rusting during shipment and storage prior to lacquer application.

115 Unlacquered panels of the treated steels, in the form of 4 × 6 inch panels, were placed, at an angle of 15°, in slotted plastic racks with $\frac{1}{2}$ inch separations between panels.

The racks were placed in a sealed humidity cabinet at 100°F and 85% relative humidity for 30 days.

- 5 Inspection of the data of Table I shows that no rusting was observed in the case of either the products of Example 1 or 2, and that there was only very slight rusting of the product of the Example 3 process (most dilute electrochemical bath, i.e. 5 g/l CrO_3).

10 *Stack Rust Resistance Test*

- 15 This is a less severe rusting test than the aforementioned rust test, but nevertheless represents conditions that would rarely, if ever, be encountered under actual service conditions.

In accordance with this test, 4 inch \times 7 inch panel samples of the treated steels, comprising five specimens of each material, were placed in a tight stack, and the stack

placed in a sealed dessicator held at ambient room temperature and 100% relative humidity for 60 days.

As shown in Table I, no rusting, under these severe conditions, was observed in the case of the product of Example 1, and only slight rusting was produced on the Example 2 and 3 products.

The processes of Examples 1—3 were conducted and the products thereof produced, on a continuous pilot line basis. Additional, commercial-scale tests were also conducted, using an aqueous electrochemical treatment bath containing, as catalyst and film promoter, 1 g/l of sulfamic acid, together with 20 g/l of chromium trioxide, the bath being maintained at a temperature of 120°F. Other test parameters, together with a characterization of the products produced, are given below in Table II.

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TABLE II

Example No.	Mill Coil Number	Line Speed, fpm	Current Density, asf		Treating Time, secs.		Coulombs per ft ²		Chromium, mg/ft ² , Coil Average	
			Anodic Pass	Cathodic Pass	Anodic Pass	Cathodic Pass	Anodic Pass	Cathodic Pass	Metallic Chromium Bottom	Cr ⁺⁺⁺ in Oxide Top Bottom
4	737119	610	125	134	0.49	2.46	62	332	0.5	9.9 10.2
5	737063	610	195	145	0.49	2.46	96	359	0.4	9.9 9.4
6	737064	610	118	84	0.49	2.46	58	208	0.4	5.7 4.8
7	737125	610	129	124	0.49	2.46	64	304	0.4	7.8 7.4

It will be seen from Table II, that, in the case of each example, a metallic chromium layer was deposited on the rapidly moving steel strip, such layer ranging in weight from 0.4 to 0.6 mg/ft² of article surface. A hydrated chromium oxide layer was also produced in each instance, and varied in weight

from 4.8 to 10.2 mg Cr⁺⁺⁺/ft² of article surface.

The results of property tests, in all respects as abovedescribed, performed upon the further examples of Table II are given in Table III.

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TABLE III

Example No.	Peel Strength lbs per $\frac{1}{4}$ " Coil Avg.		Enamel Process Adhesion Test 1 Hour Test (1) Coil Avg.		Citric Acid Test, Line Width, mm Coil Avg.		Humid Storage Test, 30 Day Grade (2) Coil Avg.		Stack Rust Test, 60 Day Grade (2) Coil Avg.	
	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom
4	22		0	0	0.1	0.1	3	2	2	2
5	25		0	0	0.1	0.1	1	1	1	1
6	36		0	0	0.1	0.1	1	2	2	2
7	27		0	0	0.1	0.1	1	1	4	4

(1) 0 = no enamel removed
10 = all enamel removed

(2) 0 = no rust
10 = heavy rust

As in the case of Table I examples, those of Tables II exhibited, as shown by the Table III data, good results in each test, indicating suitability of such products for food and beverage container manufacture.

WHAT WE CLAIM IS:

1. A method for the continuous production of coated corrosion-resistant, flat-rolled steel-base stock comprising continuously passing a flat-rolled steel-base stock through an electrochemical treating bath comprising an aqueous solution containing from 5 to 80 g/l of chromium trioxide and from 0.25 to 5 g/l of a promoter material selected from cobaltous chloride calculated as the hexahydrate and sulfamic acid, while employing the stock as cathode for the bath to provide the stock with a protective coating comprising a layer of metallic chromium adjacent to the stock surface and a layer of hydrated chromium oxide overlying the metallic chromium layer.
2. A method according to claim 1 wherein the cathodic current density is from 25 to 300 asf to provide an electrical energy input to the stock of from 50 to 1000 coulombs/ft².
3. A method according to claim 1 or 2 wherein the stock to be treated is a cleaned tin-free carbon steel black plate.
4. A method according to claims 1 to 3 wherein the solution contains from 0.25 to 1.0 g/l of cobaltous chloride (calculated as the hexahydrate) or from 0.25 to 2.0 g/l of sulfamic acid.
5. A method according to any of claims 1 to 4 wherein the electrochemical treating bath is maintained at a temperature of from 70 to 190°F.
6. A method according to any of claims 1 to 5 which includes adjusting the coulombic input to the stock in the electrochemical treating bath to obtain in the treated stock a colour corresponding to a predetermined required thickness of the hydrated chromium oxide layer.

7. A method according to any of claims 1 to 6 wherein the stock is subjected to an electrochemical anodic pre-treatment in a first treating zone.

8. A method according to claim 7 wherein the anodic treatment is carried out by immersing the stock in a bath of the same composition as is used in the treatment of the stock as cathode.

9. An electrochemical treatment bath comprising an aqueous solution containing from 5 to 80 g/l of chromium trioxide, and from 0.25 to 5 g/l of a promoter selected from cobaltous chloride (calculated as the hexahydrate) and sulfamic acid.

10. A bath according to claim 9 wherein the aqueous solution contains 0.25 to 1.0 g/l of cobaltous chloride calculated as the hexahydrate or 0.25 to 2.0 g/l of sulfamic acid.

11. Coated flat-rolled steel-base stock prepared by a method according to any of claims 1 to 8.

12. Coated stock according to claim 11 wherein the chromium layer has a weight of from 0.1 to 2.0 mg of metallic chromium per square foot of surface, and the hydrated chromium oxide layer contains from 0.1 to 30 mg of chromium values per square foot of surface.

13. A method for the continuous production of coated flat-rolled steel-base stock substantially as described hereinbefore in any one of Examples 1 to 7.

14. An electrochemical treatment bath substantially as described hereinbefore in any one of Examples 1 to 7.

15. Coated flat-rolled steel-base stock prepared substantially as described in any one of Examples 1 to 7.

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